

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 March 2004 (04.03.2004)

PCT

(10) International Publication Number
WO 2004/018738 A1

(51) International Patent Classification⁷: C25C 3/12

(21) International Application Number:
PCT/NO2003/000278

(22) International Filing Date: 15 August 2003 (15.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20024049 23 August 2002 (23.08.2002) NO

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(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

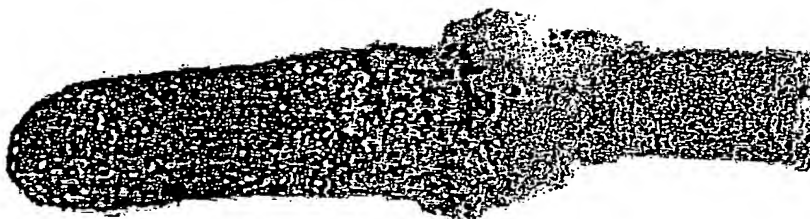
(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: A MATERIAL FOR STRUCTURAL COMPONENTS OF AN ELECTROWINNING CELL FOR PRODUCTION OF METAL



(57) Abstract: A material suitable for use for structural components in a cell for the electrolytic reduction of alumina to aluminium metal defined either by: • the formula $(A'_{1-u}A''_u)_x(B'_{1-v}B''_v)_y(C'_{1-w}C''_w)_zO_4$, in which A' and A'' are divalent elements from the group Co, Ni, or Zn, B' and B'' are trivalent elements from the group Al, Cr, Mn, or Fe, and C' and C'' are the tetravalent elements Ti or Sn. O is the element oxygen. $0 \leq u < 1$, $0 \leq v < 1$, $0 \leq w < 1$, $1 \leq x \leq 2$, $0 \leq y \leq 2$ and $0 \leq z \leq 1$, $x+y+z = 3$ and $2x+3y+4z = 8$, or • the formula $A'_{1-s}A''_sTiO_3$, in which A' and A'' are divalent elements from the group Co, Ni, or Zn. O is the element oxygen. $0 \leq s < 1$ or • the formula $A'_{1-t}A''_tO$, in which A' and A'' are divalent elements from the group Co, Ni, or Zn. O is the element oxygen. $0 \leq t < 1$.

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BTOT Rec'd PCT/PTC 23 FEB 2005

A material for structural components of an electrowinning cell for production of metal**Field of Invention**

The present invention relates to a material that can be used for structural components in a cell for the electrolysis of alumina dissolved in a fluoride containing molten salt bath by the use of essentially inert electrodes.

Background Art

Conventionally, aluminium is produced by the electrolysis of alumina dissolved in a cryolite based molten salt bath by the more than hundred years old Hall-Heroult process. In this process carbon electrodes are used, where the carbon anode is taking part in the cell reaction resulting in the simultaneous production of CO₂. The gross consumption of the anode is up to 550 kg/tonne of aluminium produced, causing emissions of greenhouse gases like fluorocarbon compounds in addition to CO₂. For both cost and environmental reasons the replacement of carbon anodes with an effectively inert material would be highly advantageous. The electrolysis cell would then produce oxygen and aluminium.

An earlier, not yet disclosed Norwegian patent application No. 2001-0927 describes the development and design of a novel electrowinning cell for aluminium production. The novel cell is based on vertical electrode technology and a two chamber electrolysis cell for separation of produced metal and evolved oxygen gas. The cell concept requires that certain structural elements are made of materials that must fulfil their functional requirements at elevated temperatures in an environment of a molten fluoride-based electrolyte. In some regions of the cell an additional requirement is that the materials must fulfil their functional requirements in contact with liquid aluminium, while in other regions the materials must fulfil their functional requirements in contact with pure oxygen gas at a pressure of about one bar.

Object of the Invention

The object of the present invention is to identify a material that is stable at an oxygen partial pressure of 1 bar at temperatures above about 680°C and has a sufficiently low solubility in the electrolyte to be used as a material for structural cell components in

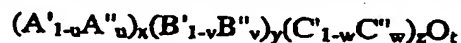
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oxidizing regions of an aluminium electrowinning cell based on substantially inert electrodes.

Summary of the Invention

The invention is the conclusion of an extensive search for materials capable of fulfilling the requirements for a material for structural cell components in oxidizing regions of an aluminium electrowinning cell based on substantially inert electrodes. The stability requirements of such a material are similar to those of an inert anode in said electrowinning cell. In the not yet published Norwegian Patent Application No. 2001-0928 the choice of possible element oxides for an inert anode is narrowed to: TiO_2 , Cr_2O_3 , Fe_2O_3 , Mn_2O_3 , CoO , NiO , CuO , ZnO , Al_2O_3 , Ga_2O_3 , ZrO_2 , SnO_2 and HfO_2 . The main requirements for a material intended for use in structural cell components are stability at 1 bar oxygen pressure at temperatures above 680°C and a low solubility in the molten electrolyte. The electrical properties are less important, but its electrical conductivity should be far less than the electrical conductivity of the electrodes and the electrolyte. The material should either itself fulfil the requirements, or it should upon contact with the molten electrolyte react to form a surface layer of an aluminate that fulfils the said requirements. Based on solubility considerations, CuO , Ga_2O_3 , ZrO_2 and HfO_2 are eliminated from the list of possible element oxides, and we are left with: TiO_2 , Cr_2O_3 , Fe_2O_3 , Mn_2O_3 , CoO , NiO , ZnO , Al_2O_3 , and SnO_2 .

The evaluation leads to a family of materials that can be expressed by the formula



in which A' and A'' are elements from the group Co, Ni, or Zn, B' and B'' are elements from the group Al, Cr, Mn, or Fe, and C' and C'' are the elements Ti or Sn. O is the element oxygen. $0 \leq u < 1$, $0 \leq v < 1$, $0 \leq w < 1$, $1 \leq x \leq 2$, $0 \leq y \leq 2$, $0 \leq z \leq 1$, and t is a number that renders the composition charge neutral.

Within this group of oxides, materials most commonly crystallize in the spinel, ilmenite or rock salt structures. In materials of the present invention that possess the

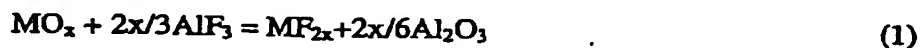
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spinel structure, $x+y+z = 3$, $2x + 3y + 4z = 8$, and $t = 4$. In materials of the present invention that possess the ilmenite structure, $x + y + z = 2$, $2x + 3y + 4z = 6$ and $t = 3$. In materials of the present invention that possess the rock salt structure, $x = 1$, $y = z = 0$, and $t = 1$.

Detailed Description of the Invention

A material suitable as an essentially inert material for structural components in the oxidizing regions of a cell for the electrolytic production of aluminium from alumina dissolved in an essentially fluoride based electrolyte where cryolite is an important ingredient, must be resistant to oxidation and dissolution in the electrolyte. A selection of the element oxides which a material for structural components can consist of, was performed based on the following criteria:

- not a gas or having a high vapour pressure at process temperature
- not converted by cryolite or AlF_3 in the cryolitic mixture, i.e. a large positive value of ΔG° for the reaction between the element oxide and AlF_3 to form the element fluoride and aluminium oxide (reaction 1).



- not converted by alumina, i.e. not a negative value of ΔG° for the reaction between the element oxide aluminium oxide and sodium fluoride to form a sodium element oxide and aluminium fluoride (reaction 2)



Of elements with the normal valence 2, the only possible elements are thus Co, Ni, Cu and Zn. Of elements with valence 3 one is left with only the elements Cr, Mn, Fe, Ga and Al. Of elements with valence 4 one is left with only the elements Ti, Zr, Hf, Ge and Sn. Cu, Ga, Zr, Hf and Ge may be eliminated from the list based on solubility considerations, and we are left with the following list of elements: Co, Ni, Zn, Al, Cr, Mn, Fe, Ti and Sn. The possible materials for structural cell components in an

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aluminium electrowinning cell based on substantially inert electrodes are thus limited to the oxides of the listed elements, or combinations of these oxides in mixed oxide compounds.

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The materials within this group can be expressed by the formula:

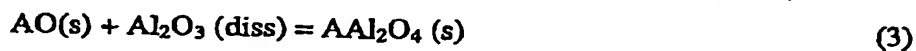


in which A' and A'' are divalent elements from the group Co, Ni, or Zn, B' and B'' are trivalent elements from the group Al, Cr, Mn, or Fe, and C' and C'' are the tetravalent elements Ti or Sn. O is the element oxygen. $0 \leq u < 1$, $0 \leq v < 1$, $0 \leq w < 1$, $1 \leq x \leq 2$, $0 \leq y \leq 2$, $0 \leq z \leq 1$, and t is a number that renders the composition charge neutral.

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Under favourable conditions the divalent oxides NiO, CoO and ZnO all react with alumina to form an essentially insoluble surface aluminate layer (reaction 3).

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where A = Co, Ni, Zn. Therefore, CoO, NiO and ZnO and solid solutions of these form one group of possible materials for structural cell components. These compositions are expressed by formula (a) with $x = 1$, $y = z = 0$, and $t = 1$. This is further illustrated in Examples 1 and 2.

20

Compounds of di- and trivalent element oxides will in this case be of the spinel structure. Spinel-like $NiFe_2O_4$, $CoFe_2O_4$, $NiCr_2O_4$ and $CoCr_2O_4$ have been suggested and extensively tested as candidates for inert anodes. In these materials, Al from the molten electrolyte has been observed to exchange with the trivalent cation to form essentially insoluble, insulating solid solutions of the type $Ni(B'_{1-v}Al_v)_2O_4$, where $0 < v < 1$, B' = Fe, Cr, Mn. This is further illustrated in Examples 3, 4, and 6. These materials are thus possible materials for structural cell components. The pure aluminates $NiAl_2O_4$, $CoAl_2O_4$ and $ZnAl_2O_4$ are also possible materials for structural cell components.

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One compound of di- and tetravalent element oxides, Zn_2SnO_4 , forms a spinel oxide. This material may in principle be used for structural cell components.

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Other stable spinel compositions that are possible materials for structural components of an aluminium electrowinning cell are achieved by substituting a divalent/trivalent spinel with a tetravalent oxide, while simultaneously adjusting the contents of the divalent and trivalent oxides in order to maintain the site and charge balance requirements of the spinel structure. This embodiment of the present invention is exemplified in Example 5.

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Spinel type materials thus form another subset of materials for structural components of aluminium electrowinning cells. These compositions are expressed by formula (a), with $x + y + z = 3$, $2x + 3y + 4z = 8$, and $t = 4$.

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NiTiO_3 , CoTiO_3 and solid solutions of these crystallize with the ilmenite structure. A cell material with the ilmenite structure may also be obtained by substitution of a trivalent element from the list of possible elements for equimolar amounts of divalent and tetravalent elements. These compositions are expressed by formula (a) with $x + y + z = 3$, $2x + 3y + 4z = 6$, and $t = 3$.

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The invention shall in the following be further described by figures and examples where:

Figure 1: Shows a photograph of a sample of a material for structural components in an electrolysis cell before and after the stability test of Example 3.

Figure 2: Shows a backscatter SEM photograph of the reaction zone of a $\text{Ni}_{1.1}\text{Cr}_2\text{O}_4$ material after 50 hours of exposure to molten fluoride electrolyte under anodic polarization.

Figure 3: Shows a backscatter SEM photograph of a NiFeCrO_4 sample after 50 hours of exposure to molten fluoride electrolyte under anodic polarization.

Figure 4: Shows a backscatter SEM photograph of a sample of $\text{Ni}_{1.5+x}\text{FeTi}_{0.5-x}\text{O}_4$ after the stability test of Example 5.

Figure 5: Shows a backscatter SEM photograph of a $\text{Ni}_{1.01}\text{Fe}_2\text{O}_4$ sample after 30 hours of exposure to molten fluoride electrolyte under anodic polarization.

Example 1:

Test of the stability of a NiO sample anodically polarized in a molten fluoride electrolyte.

A cermet with 75 wt% NiO and 25 wt% Ni was prepared using INCO Ni powder type 210, and NiO from Merck, Darmstadt. The material was sintered in argon atmosphere at 1400°C for 30 min.

The sample was exposed to a molten fluoride bath under anodic polarization in order to ensure a partial pressure of 1 bar oxygen on the sample surface. The electrolyte was contained in an alumina crucible with inner diameter 80 mm and height 150 mm. An outer alumina container with height 200 mm was used for safety, and the cell was covered with a lid made from high alumina cement. In the bottom of the crucible a 5 mm thick TiB_2 disc was placed, which made the liquid aluminium cathode stay horizontal. The electrical connection to the cathode was provided by a TiB_2 rod supported by an alumina tube to avoid oxidation. A platinum wire provided electrical connection to the TiB_2 cathode rod. A Ni wire provided for the electrical connection to the anode. The Ni wire and the anode above the electrolyte bath was masked with an alumina tube and alumina cement to prevent oxidation.

340 g Al, (99.9% pure), from Hydro Aluminium was placed on the TiB_2 disc at the bottom of the alumina crucible.

5 The electrolyte was made by adding to the alumina crucible a mixture of :

532 g Na_3AlF_6 (Greenland cryolite)

105 g AlF_3 (from Norzink, with about 10 % Al_2O_3)

35 g Al_2O_3 (annealed at 1200°C for some hours)

21 g CaF_2 (Fluka p.a.)

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The sample of the material for structural cell components was suspended above the electrolyte during heating of the cell. The temperature was maintained at 970°C during the whole experiment. The sample of the material for structural cell components was lowered into the molten electrolyte and polarized anodically with a current density of 750 mA/cm^2 based on the bottom end cross sectional area of the sample. The real current density was somewhat lower because the side surfaces of the anode were also dipped into in the electrolyte.

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The experiment lasted for 8 hours. XRD (X-ray diffraction) analysis of the anode after the experiment showed that the Ni metal was oxidized to NiO and the anode material was covered by an dense, protective, insulating layer of NiAl_2O_4 .

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Example 2:

Test of the stability of a ZnO sample anodically polarized in a molten fluoride electrolyte.

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ZnO was doped with 0.5 mol% $\text{AlO}_{1.5}$. Two Pt wires were pressed into the material in the longitudinal axis of the ZnO anode and acted as electrical conductors. The material was sintered at 1300°C for 1 hour.

30

The stability test was performed in the same manner as described in Example 1. The amounts of electrolyte and aluminium were the same. The temperature was 970°C. The current density was set to 1000 mA/cm^2 based on the bottom end cross sectional area of the sample. The electrolysis experiment lasted for 24 hours. XRD (X-ray diffraction)

analysis of the sample after the electrolysis experiment showed that ZnO had been converted to ~~ZnAl₂O₄~~ during electrolysis.

Example 3:

5 **Test of the stability of a $\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$ sample anodically polarized in a molten fluoride electrolyte.**

The starting powder was prepared by a soft chemistry route. The appropriate amounts of $\text{Ni}(\text{NO}_3)_2$, and $\text{Cr}(\text{NO}_3)_3$ were complexed with citric acid in dilute nitric acid. After evaporation of excess water, the mixture was pyrolysed and calcined at 900°C for 10
10 hours. The sample was cold isostatically pressed at 200 MPa, then sintered at 1440°C for 3 hours. The material was found by XRD to possess the spinel structure.

The stability test was performed in the same manner as described in Example 1, but a
15 platinum wire provided electrical connection to the sample. The platinum wire to the sample was protected by a 5 mm alumina tube. When the electrolysis started the anode was dipped approximately 1 cm into the electrolyte. A photograph of the sample before and after electrolysis is shown in Figure 1.

20 The electrolyte, temperature and current density were the same as described in Example 2.

The stability test lasted for 50 hours. After the experiment the sample was cut, polished and examined in SEM (Scanning Electron Microscope). A reaction zone could be seen between the $\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$ - material and the electrolyte. Figure 2 shows the backscatter
25 SEM photograph of the reaction zone. On the photograph one can see a reaction zone that has propagated along the grain boundaries of the $\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$ material. The white particles are NiO.

30 In the table below the relative EDS analysis results are reported. Ni, Cr, Al, and O were the only elements detected. The aluminium present in the interior of the grains might be due to the preparation of the sample for analysis.

Relative comparison between the elements Ni, Cr and Al:

Element:	Atom % in the centre of the grains in Figure 2:	Atom % in the reaction zone in grain boundaries in Figure 2:
Ni	33	47
Cr	66	8
Al	1	45

The SEM analysis shows that the reaction product consisted of a material where the chromium atoms were partly exchanged with aluminium atoms as described by the formula $\text{NiCr}_{2-x}\text{Al}_x\text{O}_4$ where x varies from 0 to 2. The reaction product forms an insulating coating.

Example 4:

Test of the stability of a NiFeCrO_4 sample anodically polarized in a molten fluoride electrolyte.

The starting powder was prepared by a soft chemistry route. The appropriate amounts of $\text{Ni}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and $\text{Cr}(\text{NO}_3)_3$ were complexed with citric acid in dilute nitric acid. After evaporation of excess water, the mixture was pyrolysed and calcined at 900°C for 10 hours. The sample was cold isostatically pressed at 200 MPa, then sintered at 1600°C for 3 hours. The material was found by XRD to possess the spinel structure.

The stability test was performed in the same manner as described in Example 3. The amounts of electrolyte and aluminium were the same. The current density was set to 1000 mA/cm² based on the cross sectional area of the rectangular sample. The experiment lasted for 50 hours. Examination of the sample after exposure to molten fluorides under anodic polarization showed a several micron thick reaction layer where Cr in the material was partly exchanged with Al atoms. A backscatter SEM photograph of the reaction layer is shown in Figure 3. Light grey areas consist of original NiFeCrO_4 material. Medium grey area contains almost no Cr atoms and a much lower content of Fe.

EDS analysis of the medium grey reaction layer shown in Fig. 3 compared to original NiFeCrO_4 material and the inner of the anode light grey area also shown in Fig. 3 are summarized in table below. The only elements detected were Ni, Cr, Fe, Al and O.

Comparison of the relative amounts of Cr, Fe, Ni and Al:

Element:	Atom % in the original NiFeCrO_4 material. Light grey area in Fig. 3.	Atom % in the reaction layer after the test. Medium grey area in Fig. 3.
Cr	33.3	0
Fe	33.3	16
Ni	33.3	35
Al	0	49

The conclusion of the stability test is that the NiFeCrO_4 material reacts with alumina in the electrolyte and forms a dense, essentially insoluble, insulating layer of $\text{NiFe}_{1-x}\text{Al}_x\text{O}_4$.

Example 5:

Test of the stability of a $\text{Ni}_{1.5+x}\text{FeTi}_{0.5-x}\text{O}_4$ sample anodically polarized in a molten fluoride electrolyte.

The starting powder was prepared by a soft chemistry route. The appropriate amounts of $\text{Ni}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ and $\text{TiO}_3\text{H}_{14}\text{C}_{10}$ (titanyl acetylacetonate) were complexed with citric acid in dilute nitric acid. After evaporation of excess water, the mixture was pyrolysed and calcined at 900°C for 10 hours. The sample was cold isostatically pressed at 200 MPa, then sintered at 1500°C for 3 hours. The material was found by XRD to possess the spinel structure.

The stability test was performed in the same manner as described in Example 3. The amounts of electrolyte and aluminium were the same. The current density was set to 1000 mA/cm^2 based on the cross sectional area of the rectangular sample. The experiment lasted for 30 hours. After the experiment the sample was cut, polished and examined in SEM. The backscatter photo in Fig. 4 shows the end of the sample facing the cathode. In this experiment no reaction layer was detected on the $\text{Ni}_{1.5+x}\text{FeTi}_{0.5-x}\text{O}_4$ anode after 30 hours.

Example 6:

Test of the stability of a $\text{Ni}_{1.01}\text{Fe}_2\text{O}_4$ sample anodically polarized in a molten fluoride electrolyte.

The starting powder was prepared by a soft chemistry route. The appropriate amounts of $\text{Ni}(\text{NO}_3)_2$, and $\text{Fe}(\text{NO}_3)_3$ were complexed with citric acid in dilute nitric acid. After evaporation of excess water, the mixture was pyrolysed and calcined at 900°C for 10 hours. The sample was cold isostatically pressed at 200 MPa, then sintered at 1450°C for 3 hours. The material was found by XRD to possess the spinel structure.

The stability test was performed in the same manner as described in Example 3. The amounts of electrolyte and aluminium were the same. The current density was set to 1000 mA/cm² based on the cross sectional area of the rectangular anode. The experiment was stopped after 30 hours. After the experiment the sample was cut, polished and examined in SEM. Figure 5 shows a backscatter photograph of the sample at the end facing the cathode. An approximately 10 micron thick reaction layer is seen.

A line scan EDS analysis was done to examine whether the layer was a reaction layer or electrolyte adhering to the surface. The line scan indicated a thin layer of bath components, and then a reaction layer of approximately 10 micron thickness. In the interior of the anode and in the reaction layer only oxygen was detected in addition to Ni, Fe and Al. The results are reported in the table below:

Comparison of the relative amounts of Ni, Fe and Al:

Element:	Atom % of element in the interior of the anode shown in Figure 5 and analysed with line scan EDS:	Atom % of element in the reaction layer as shown in Figure 5 and analysed with line scan EDS:
Ni	33	30
Fe	67	30
Al	0	40

In the 10 micron thick reaction layer the iron atoms were partly exchanged with aluminium atoms to form an essentially insoluble, insulating layer of $\text{NiFe}_x\text{Al}_{1-x}\text{O}_4$.

1 Claims (revised)

1. A material for manufacture of structural components, excluding electrodes, in a cell for electrolytic reduction of alumina to aluminium,

characterised by
the formula



in which t is essentially 1, 3 or 4, O is the element oxygen, A' and A'' are elements from the group Co, Ni, or Zn, B' and B'' are elements from the group Al, Cr, Mn, or Fe and C' and C'' are the elements Ti or Sn, $0 \leq u < 1$, $0 \leq v < 1$, $0 \leq w < 1$, $1 \leq x \leq 2$, $0 \leq y \leq 2$, $0 \leq z \leq 1$; when t is essentially 1, $y = 0$ and $z = 0$, when t is essentially 3, $y = 0$, $w = 0$ and C' denotes the element Ti.

2. A material in accordance with claim 1,

characterised in that
the cation A' is essentially divalent Ni, u is essentially 0 and x is essentially 1.

3. A material in accordance with claim 1,

characterised in that
the cation B' is essentially trivalent Al, the cation B'' is essentially trivalent Fe and y is essentially 2.

4. A material in accordance with claim 1,

characterised in that
the cation A' is essentially divalent Ni, the cation B' is essentially tetravalent Ti, and u, v and z are essentially 0.

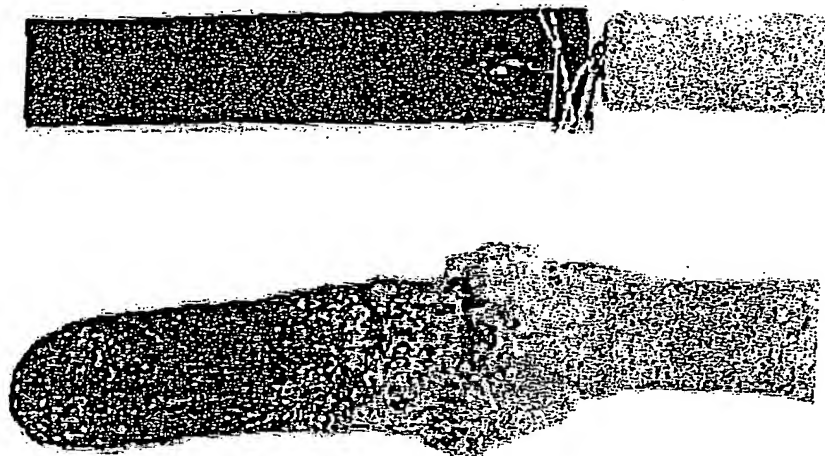


Fig. 1

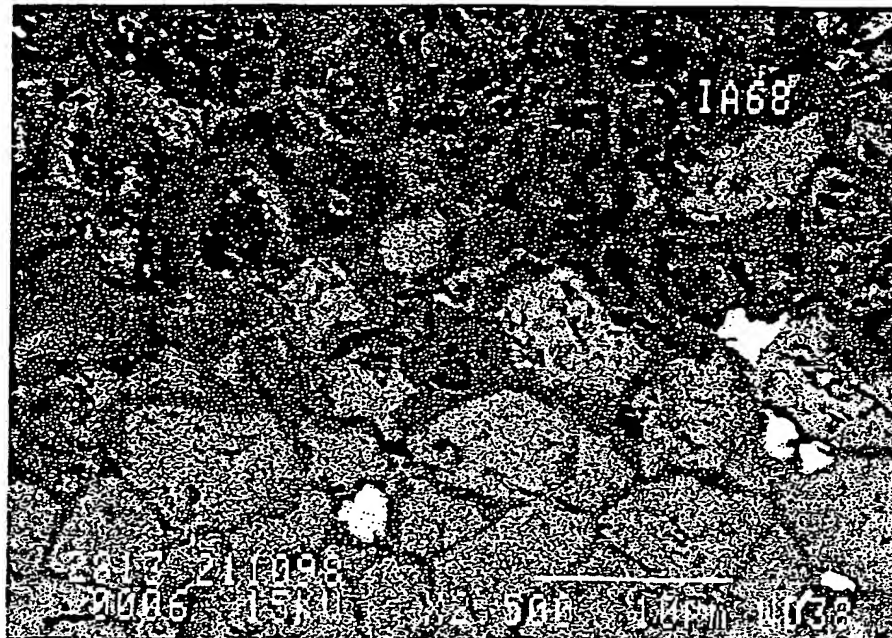


Fig. 2

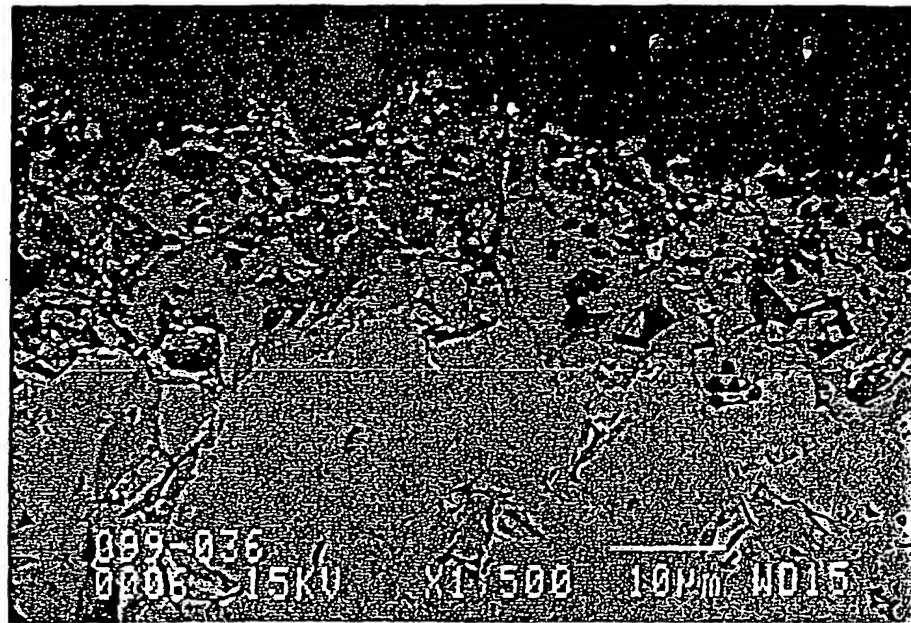


Fig. 3

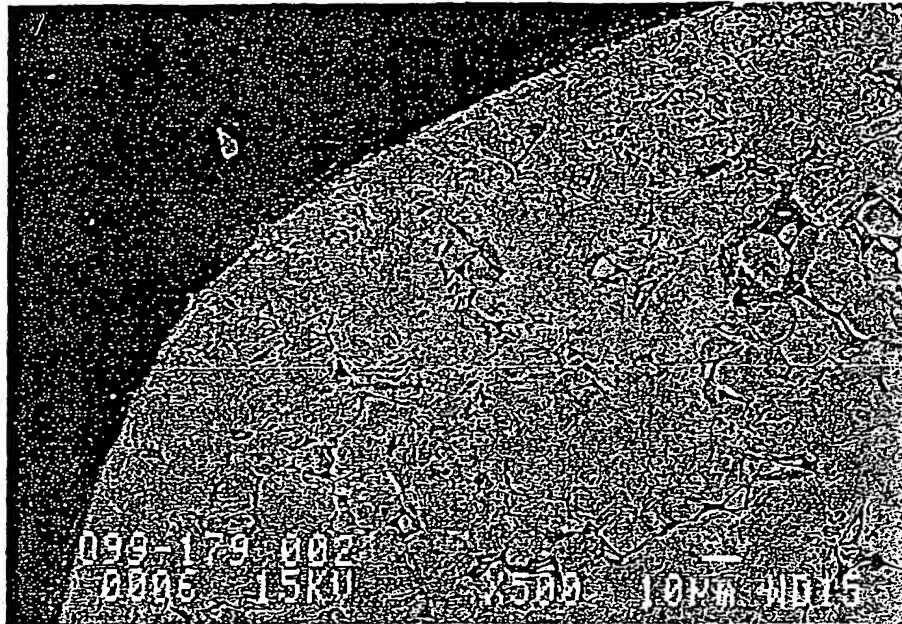


Fig. 4

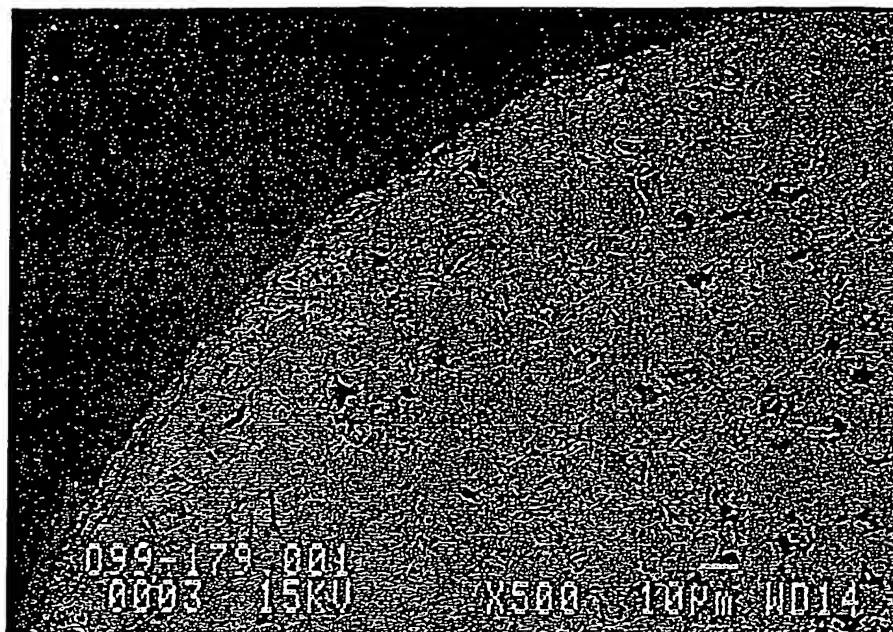


Fig. 5

Abstract

A material suitable for use for structural components in a cell for the electrolytic reduction of alumina to aluminium metal defined either by:

- the formula $(A'_{1-u}A''_u)_x(B'_{1-v}B''_v)_y(C'_{1-w}C''_w)_zO_4$, in which A' and A'' are divalent elements from the group Co, Ni, or Zn, B' and B'' are trivalent elements from the group Al, Cr, Mn, or Fe, and C' and C'' are the tetravalent elements Ti or Sn. O is the element oxygen. $0 \leq u < 1$, $0 \leq v < 1$, $0 \leq w < 1$, $1 \leq x \leq 2$, $0 \leq y \leq 2$ and $0 \leq z \leq 1$, $x+y+z = 3$ and $2x+3y+4z = 8$,

or

- the formula $A'_{1-s}A''_sTiO_3$, in which A' and A'' are divalent elements from the group Co, Ni, or Zn. O is the element oxygen. $0 \leq s < 1$

or

- the formula $A'_{1-t}A''_tO$, in which A' and A'' are divalent elements from the group Co, Ni, or Zn. O is the element oxygen. $0 \leq t < 1$.

(Fig. 1)